DEVELOPMENT OF δ AND γ BANDS OF NITRIC OXIDE IN ACTIVE NITROGEN AND LYMAN BANDS IN HELIUM-NITROGEN MIXTURE

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Plate V

ABSTRACT. The doublet structure of 0-0, 0-1, 0-2 and 0-3 bands of δ system of nitric oxide as observed in active nitrogen by a one metre normal incidence vacuum spectrograph is described.

The vibrational structure of 1,0 and 2,0 bands of γ system has been measured.

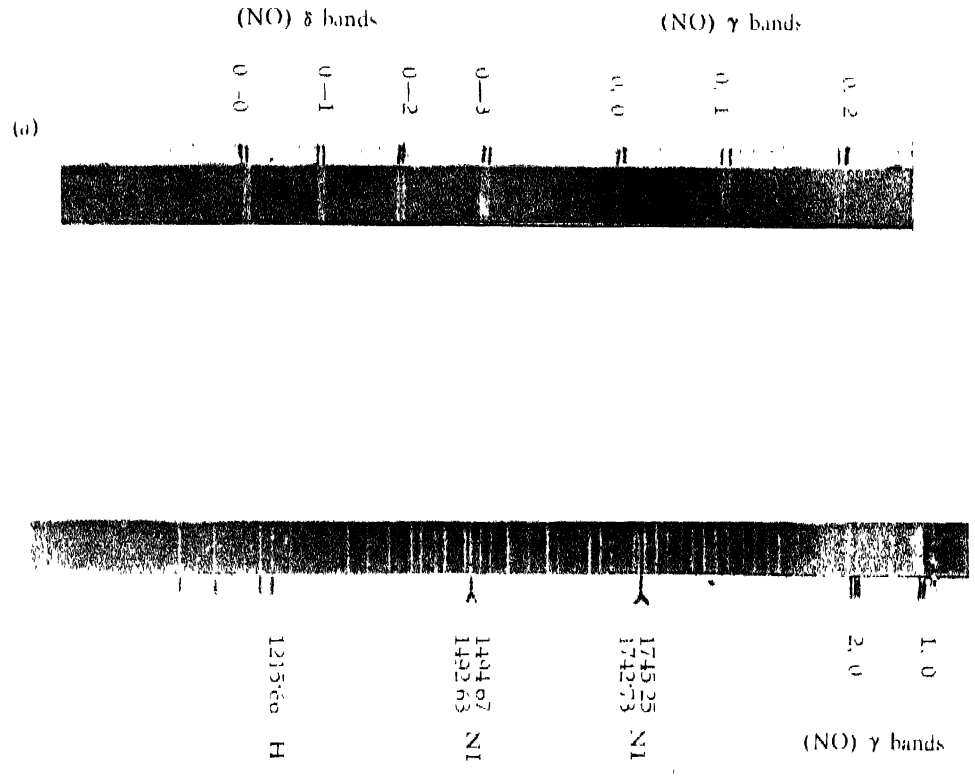
It is found that whereas δ and γ band systems are prominently present, β bands of nitric oxide lying in the vacuum region, are particularly absent in the afterglow of nitrogen under the conditions of the experiment.

Lyman-Birge-Hopfield bands of nitrogen have been developed in a mixture of helium and nitrogen. Three new bands of the system—(6,13), (0,8) and (4,9) are reported.

The band spectrum of NO molecule consists of β, γ and δ systems of bands, which are easily developed in the afterglow of nitrogen containing oxygen as an impurity. The character of bands excited in active nitrogen is characteristic of a low temperature radiating source. The number of lines are few and the heads appear prominently and the v'' progression corresponding to $v'=0$ is particularly strong in emission.

The δ bands were first observed by Knauss (1928) in active nitrogen. Six emission band heads degraded towards the short wavelength side corresponding to single progression $v'=0$, $v''=0$, 1, 2, 3, 4, 5 were recorded by him between λ 2320 and λ 1913, with a one metre vacuum grating spectrograph, using oil coated plates and a slit width of 0.25 mm. The 0,0 band lying at λ 1913 was indentified as the one previously reported by Leifson (1926) at λ 1910.6 as absorption band due to NO. Because of the large width of the slit and the use of the oil coated plates, the structure of these bands could not be observed.

Later, Schmidt (1930) observed the doublet structure of these bands with large quartz spectrograph E_1, and analysed the rotational structure of 0-3, 0-4 and 0-5 bands. His analysis showed that these bands correspond to $^2\Sigma \rightarrow {}^2\Pi_{\frac{1}{2}}, \frac{3}{2}$ transitions, the latter being the ground level. Each sub-level gave rise to two sub-heads corresponding to P and Q branches. The values of 0,0 Q heads for each sub-level have been computed from this data, but no further attempt seems to have been made to photograph and measure the doublet structure of the 0-0 0-1, 0-2 and 0-3 band heads of this system lying in the vacuum region.



(N_2) Lyman Birge Hopfield bands

During the course of a work reported in this journal on active nitrogen in the Schumann region, the author obtained the first four bands of the progression $v''=0, 1, 2, 3, v'=0$ very prominently in one of the spectrograms taken with a one metre normal incidence vacuum spectrograph. The doublet structure was distinct and the results of the measurements and the corresponding values of Knauss and Schmidt are given for comparison in Table I.

TABLE I

λ in vacuum of δ bands of NO

v', v''	Present values	Intensity	Knauss values	Schmidt values
0,0	Q_1	1910.2 (4)		
		1913.5 (3)	1913	
	Q_2	1914.6 (3)		
0,1	Q_1	1980.9 (5)		
		1984.5 (3)		
	Q_2	1985.6 (4)	1987	
0,2	Q_1	2056.0 (4)		
		2059.8 (2)		
	Q_2	2061.3 (3)	2062	
0,3	Q_1	2135.8 (4)		2135.5 Q1
		2140.1 (2)		
	Q_2	2141 4 (3)	2142	2141.0 Q2

In Table II, wave numbers of the various heads are given. The differences represent the separations of the vibrational levels in the initial electronic state.

TABLE II

v', v''	0	1	2	3	Head	Transition
	53251 (1869)	50482 (1844)	48638 (1817)	46821	Q_1	$^2\Sigma-^2\Pi_{\frac{1}{2}}$
0	52260 (1869)	50391 (1843)	48548 (1821)	46727		
	52230 (1867)	50363 (1843)	48520 (1822)	46698	Q_2	$^2\Sigma-^2\Pi_{\frac{3}{2}}$
$\Delta\nu$	(1868)	(1843)	(1820)			

The intensities are relative visual estimates. The plate was measured on a Hilger comparator a number of times and the estimated error is not considered to be more than 0.1 Å.

In the same spectrogram a number of bands of γ system of NO are present, plate V (*a*). This system has been thoroughly studied by a large number of workers. However, it appears from the Identification Tables of Molecular Spectra (1941) by Pearse and Gaydon that, for the bands of this system lying below λ 2200, values corresponding to only one single head are available. In this spectrogram the doublet structure is definitely brought out though the bands are diffuse. Consequently, readings approximately at the centre of each head could only be taken.

In another spectrogram plate V (*b*) obtained by passing an uncondensed discharge in a mixture of helium and nitrogen, the vibrational structure of (1,0) and (2,0) bands of γ system has come out very well. Table III gives the measured wave-lengths and the corresponding wave numbers of the various heads of these bands along with the previous values as given in the Identification Tables of Pearse and Gaydon (1941):

TABLE III

v', v''	λ in Å	Intensity visual estimate	ν in cm.$^{-1}$	Head	Transition	Previous values
2,0	2047.0	2	48853	Q1	$A^2\Sigma - X^2\Pi_{\frac{1}{2}}$	2060
	2048.3	2	48822	P1		
	2052.2	1	48728	Q2	$A^2\Sigma - X^2\Pi_{\frac{3}{2}}$	
	2053.3	1	48702	P2		
1,0	2148.5	4	46544	Q1	$A^2\Sigma - X^2\Pi_{\frac{1}{2}}$	2156
	2149.5	4	46522	P1		
	2154.0	2	46426	Q2	$A^2\Sigma - X^2\Pi_{\frac{3}{2}}$	
	2155.3	2	46397	P2		

This plate shows prominently the well-known band system of nitrogen molecule lying in the vacuum ultra-violet and first observed by Schumann (1903). A large number of these bands degraded to the red and lying between λ1300-λ1900 were measured by Lyman (1911). Birge and Hopfield (1928) obtained this system of bands both in absorption and emission. As a result of their vibrational analysis this system was found to be due to a $^1\Pi \rightarrow {}^1\Sigma$ transition, the latter electronic state being the ground level X of the neutral nitrogen molecule. In all their experiments purified nitrogen, *i.e.* commercial nitrogen passed over heated copper at a pressure which never exceeded 0.002 mm. was used. The most prominent impurity in these spectra was that of nitric oxide (NO). Subsequently, nitrogen was obtained by exploding sodium oxide when CO, H_2 and NO appeared as impurities.

In the present experiment pure helium at a pressure of 8 m.m. was mixed with 1% nitrogen in a Pyrex glass discharge tube 140 cm. long, 2.2 cm. in diameter, fitted with three aluminium electrodes A, B and C. The tube was

sealed end-on without any window to the one-metre normal incidence vacuum spectrograph. A schematic diagram of the apparatus is shown in Fig. 1.

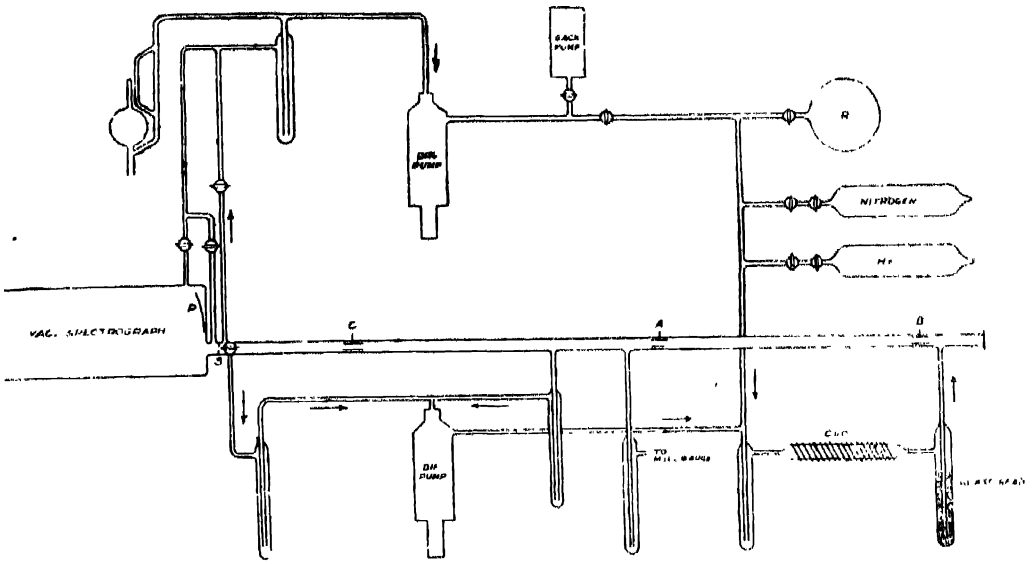


FIG. 1

Two four-stage mercury diffusion pumps maintained a difference of pressure between the discharge tube and the spectrograph. The pressure in the discharge tube was about 8 mm. while in the spectrograph it was about .01 mm. Six liquid air traps kept the discharge free from mercury and other impurities. An electrically heated quartz tube containing CuO eliminated hydrogen. A two-litre reservoir R in the main stream kept the pressure in the tube steady. The other parts are self-explanatory. For excitation of the discharge the secondary of a 15,000 volts, 450 watts transformer was connected to the terminals A and C of the discharge tube. The exposure time was one hour on a Schumann plate prepared in the Laboratory from photographic gelatine Batch 73-400 from Eastman Kodak Co.

The following impurity lines were used as comparison standards:—

1215.66 HI, 1492.63 NI, 1494.67 NI.

1742.73 NI, 1745.25 NI.

The plate was measured a number of times on two comparators (Hilger and Carl Leiss) and the mean values obtained. The intensities are the visual estimates on an arbitrary scale of 0-10. Table IV gives the mean values compared with the Birge-Hopfield values:

The values given in brackets for 6-13, 0-8 and 4-9 band heads are the computed values as calculated by Birge and Hopfield.

Some of the interesting results brought out by these experiments may be noted as follows:

(1) No attempt was made to get NO bands. The exposure was given only to get the emission spectrum of the nitrogen afterglow. A little trace of oxygen

TABLE IV

Measured values of λ in Å	Intensity	Birge-Hopfield values	Intensity	V′−V″
2007.0	2	2007.4	2	3-11
1989.5	1	1989.9	1	2-10
1984.9	1	—	--	—
1980.2	1	(1980.06)	—	6-13
1973 5	1	1973 1	0	1-9
1962.4	1	1963.1	1	5-12
1955.1	1	(1955.96)	—	0-8
1944.7	2	1944.8	4	4-11
1927.6	2	1927.8	4	3-10
1910.9	3	1911.0	4	2-9
1894.0	2	1894 3	2	1-8
1870.7	1	1871.0	4	4-10
1853.9	3	1853.9	4	3-9
1836.9	4	1837.2	5	2-8
1820.6	4	1820.8	5	1-7
1804.5	2	1804.7	3	0-6
1800.1	1	(1800.93)	—	4-9
1784.9	1	1784.6	3	3-8
1768.0	4	1768.1	6	2-7
1751.9	5	1751.9	7	1-6
1736.0	4	1736.2	5	0-5
1702.9	2	1703.3	4	2-6
1687.2	6	1687.3	9	1-5
1671.7	6	1671.7	8	0-4
1657.5	1	1657.7	4	3-6
1626.4	2	1626.5	6	1-4
1611.4	6	1611.3	9	0-3
1600.3	1	1599.7	4	3-5
1584.1	2	1584.4	5	2-4
1576.3	1	1575.9	3	5-6
1554.2	6	1554.3	9	0-2
1529.6	3	1529.9	5	2-3
1515.0	3	1515.2	5	1-2
1500.7	5	1500.7	7	0-1
1464.0	6	1464.1	8	1-1
1450.3	3	1450.1	5	0-0
1444.0	2	1444.3	4	3-2
1429.7	3	1429.9	6	2-1
1415.7	4	1415.9	6	1-0
1412.3	2	1411.6	5	4-2
1383.7	5	1383.8	8	2-0
1953.5	4	1353 6	8	3-0
1325.7	3	1325.2	6	4-0
1311.5	1	1312.3	4	6-1
1298.9	1	1298.4	5	5-0
1226.3	1	1226.6	abs.	8-0

as an impurity was therefore responsible for the formation of NO and the development of γ and δ systems of NO bands.

(2) The doublet structure of 0,0, 0,1, 0,2, 0,3 δ bands has, so far as the author is aware, come out for the first time. Each band consists of two definite heads Q_1, Q_2 with a mean wave number difference of about 120 cm.$^{-1}$ corresponding to the interval $^2\Pi_{\frac{3}{2}} - {}^2\Pi_{\frac{1}{2}}$ of the ground state. The shorter wave-length head corresponding to $^2\Sigma - {}^2\Pi_{\frac{1}{2}}$ transition forms the Q_1 head and $^2\Sigma - {}^2\Pi_{\frac{3}{2}}$ transition forms the Q_2 head. In all the bands the Q_1 head is stronger than the Q_2 head. Moreover, whereas the Q_1 head is followed by an unresolved rotational structure up to about 4 Å towards the violet side, the Q_2 head is much sharper and there is a clear gap of about 30 cm.$^{-1}$ after which a fine structure starts towards the

shorter wave-length side. The central reading given in the tables I and II for each band corresponds to the long wave-length edge of this structure.

(3) The doublet structure of 0-0, 1-0, 2-0, 3-0, 0-1, 0-2 and 1-4 bands of γ system of NO could be roughly measured. Usually in active nitrogen the relative intensity of β and γ bands is of the same order. The strongest bands of β system, however, do not lie in the vacuum region. The 2-4 and 3-4 bands of β system lying at about λ 2490 and 2430 were searched for in the spectrogram but there was not the faintest impression of these bands. In this case, the γ bands were thus present exclusive of the β bands in this region. Possibly if the partial pressure of oxygen and, therefore, of NO were increased, the β bands would have made their appearance. One may draw the conclusion that under the conditions of the experiment, that is when the partial pressure of NO is extremely small, the maximum number of NO molecules are in the C $^2\Sigma$ state corresponding to the upper state of δ bands, a smaller number of them in A $^2\Sigma$ state, the upper state of γ bands, but comparatively very much smaller number of molecules in the B $^2\Pi$ state particularly corresponding to the vibrational states 2-4 and 3-4 giving rise to the β bands in the vacuum region.

(4) The vibrational structure of 1,0 and 2,0 bands of γ system has been measured. Values for both the P and Q heads for the two sub-levels are given. The Q heads show a prominent unresolved rotational structure towards the shorter wave-length side.

(5) Lyman-Birge Hopfield bands have been developed in nitrogen containing excess of helium. Three new bands observed at λ 1980.2 (6,13), 1955.1 (0,8), and 1800.1 (4,9) are reported. In Birge and Hopfield spectrograms bands such as 1-3, 2-5, 4-3, 4-8, 5-7, 5-10, 6-2, 6-4 and 6-9 were missing. The author was interested in finding out if some of these missing bands could be developed in nitrogen-helium mixtures. This plate does not show any one of the above-mentioned missing bands.

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